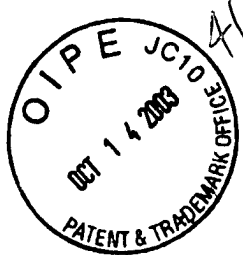


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TC 1700

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: Bonnie R. Hames )  
Serial No.: 10/031,208 ) Art Unit No.: 1724  
Filing Date: May 24, 2002 ) Examiner: Chester T. Barry  
Entitled: Phenol Removal Pretreatment ) Atty. Docket: NREL 98-21  
Process )

CERTIFICATE OF MAILING UNDER 37 CFR § 1.10

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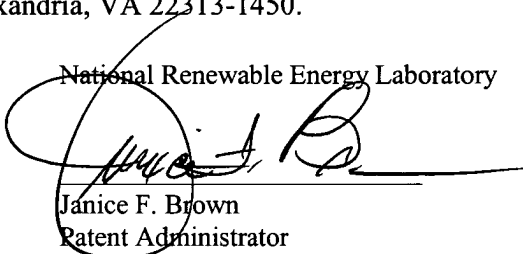
Date of Deposit 14 October 2003

I hereby certify that the following attached items:

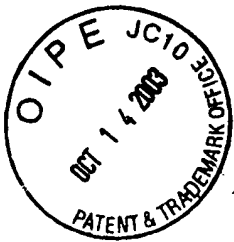
- (1) Amendment Under 37 CFR 1.121 [1 pg]
- (2) Amended Specification pages 3, 4, 5, 6, [4 pgs]
- (3) Postcard receipt

are being deposited in the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and addressed to: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

National Renewable Energy Laboratory

  
Janice F. Brown  
Patent Administrator

1617 Cole Boulevard  
Golden, CO 80401  
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## AMENDMENT UNDER 37 CFT 1.121

Commissioner For Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

To Whom It May Concern:

The Applicant is responding to the Office Action dated September 11, 2003. Consistent with the Revised Amendment Practice, 37 CFR 1.121, attached are the revised pages of the specification with minor informalities corrected as follows:

<u>Page</u>	<u>Lines</u>
3	4, 5, 7, 13, 14, 15
4	12
5	3, 20
6	8

Applicant's attorney respectively solicits a Notice of Allowance in this application. Should the Examiner have any questions that would expedite the prosecution of this case to allowance, please feel free to contact the undersigned at the number listed below.

Dated: October 14, 2003

Respectfully Submitted,

Paul J. White, Reg. No. 30,436  
National Renewable Energy Laboratory  
1617 Cole Boulevard  
Golden, CO 80401  
Telephone: (303) 384-7575

invention belongs. Although any methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present invention, the preferred methods and materials are now described.

As used herein the term ~~Aphenolic@~~ "phenolic" is an adjective meaning a member of the class of phenols. ~~Aphenols@~~ "Phenols" means the class of aromatic compounds in which one or more hydroxyl groups are attached directly to a benzene ring. Examples of phenols include phenol, cresol and resorcinol. ~~Abiomass~~ "Biomass-derived phenols@" include the compounds known as guaiacol, syringol, isoeugenol and vanillin.

The process uses a metal oxide, such as titanium dioxide, for the selective adsorption and removal of phenolic compounds from an aqueous solution, such as a biomass-hydrolyzate medium. Dissolved sugars in the solution are thereby concentrated. Adsorption is highly selective, and provides an efficient method for the fractionation of a biomass-hydrolyzate, 90% of the ~~hydrolyzate=s~~ hydrolyzate's dissolved lignin being removed without a measurable decrease in the ~~solution=s~~ solution's dissolved sugar concentration. Selectivity is attributable to the metal ~~oxide=s~~ oxide's preferential binding with those oxygen molecules which are located on adjacent (ortho) carbons of the aromatic ring structures.

With reference now to Figure 1, the starting material is a biomass hydrolysis liquor 1. The hydrolysis liquor 1 is mixed in contacting step 4, as a suspension, with a metal oxide 2, such as a Norton Chemical Process Products Corporation, Akron, Ohio high-surface-area TiO<sub>2</sub> 1/8 " extrudate type XT25384. High separation efficiency is generally achieved by using an amount or weight (wt) of TiO<sub>2</sub>, which is twice the estimated phenol content of the liquor. This ratio varies, however, with the form, source, active surface area, and liquid-contact surface area of the TiO<sub>2</sub>, to be used. Separation efficiency also varies with the age of the aqueous mixture and source of the biomass. Producing hydrolyzate under conditions of high severity also reduces the separation efficiency.

Selective adsorpting step 6 is accomplished using all grades of TiO<sub>2</sub>. The rate and efficiency of the adsorption of aromatic compounds with TiO<sub>2</sub> is dependent upon the TiO<sub>2</sub> active surface area. Anatase titanium dioxide, preferable to the rutile form, may be of any high-

surface-area formulation, including powders, thin-films, sol-gel crystals, and extruded pellets. Vanadium oxide and zirconium oxide, and at pH in a range of greater than 7.0 manganese dioxide, silica, and alumina, may also be used.

Depending upon the quantity of the aromatic compounds to be removed, a batch reaction vessel or plug flow reactor may be used as an adsorption vessel. In a batch reactor, the retention time is preferably 30 minutes. In a plug flow column, the retention time is preferably 15 minutes. These retention times typically result in a separation of up to 90-weight % of the aromatics from the hydrolyzate 1. Longer retention times are desirable where the separation is carried out at a low pH. For example, the adsorption is slower in the pH range of 2 - 6 and occurs more rapidly when the pH is in the range of 7 -10.

The process retains its efficiency and selectivity throughout a temperature in the range of 20°C-90°C. Performing the selective adsorption under conditions of elevated temperature and pH does not affect adsorption selectivity relative to the carbohydrate fraction.

However, above pH 6, some carbohydrate degradation products, such as 5-(hydroxymethyl) furfural and furfural, are also adsorbed on the metal oxide surface. At combinations of higher pH and temperature some entrainment of soluble salts occurs on the metal oxide surface when the hydrolyzate 1 and metal oxide 2 mixture contains salts having a lower solubility at higher temperatures, such as calcium sulfate. Raising both the temperature and the pH does not affect the adsorption selectivity of this process for lignin. After contacting the hydrolyzate and metal oxide, adsorption preferably includes agitating the mixture for a time sufficient to allow the colloidal particles to deposit on the TiO<sub>2</sub> particulate surfaces, as indicated by a clearing of the suspension, and allowing the suspension to settle at room temperature for 1 hour. The adsorbed complex is then separated in separation step 8. Separation may be accomplished using a glass-fiber filter. The carbohydrate fraction of the hydrolysis liquor is contained in the sugars filtrate 10.

A unique aspect of the invention is its high separation selectivity for lignin in an aqueous hydrolysis liquor having an excess of monomer sugars. More than 90% of the solubilized lignin can be removed from the hydrolyzate without any loss of glucose or xylose. When using TiO<sub>2</sub>

extruded pellets as an adsorbent, a slight concentration effect is observed during the adsorption process. This effect may be due to hydration of the metal oxide and the exclusion of sugars from the metal ~~oxide-s~~ oxide's surface. Solid state nuclear magnetic resonance analysis of lignin model compounds, adsorbed on the TiO<sub>2</sub> surface, has suggested that the lignin selectivity is due, at least in part, to an affinity of titanium for adjacent oxygen molecules which are located on the aromatic ring structure of the adsorbed substrates. It has been found that, through chemical shifts in <sup>13</sup>C nmr between lignin model compounds both before and after complexation with titanium alkoxides, these molecules bind preferentially through the phenolic oxygen and the oxygen of the adjacent methoxyl group. The biomass-derived aromatic substituents have two main substitution patterns, commonly known as guaiacyl and syringyl, which contain the functional groups necessary for the selective fractionation. Although titanium, and many other transition metals, are known to be highly oxyphilic, the affinity of this functionality for these metal oxides is so strong that in the presence of these aromatic compounds, even highly oxygenated carbohydrate-derived compounds are excluded from the metal oxide surface.

The process may also include a regeneration step 14. In this step, the TiO<sub>2</sub> adsorbents are easily regenerated using combustion of the complex at 400°C for 15 minutes. An estimated 100-500 regeneration cycles may be utilized without a significant reduction in adsorption capacity or selectivity. It is preferred to regenerate the TiO<sub>2</sub> at a temperature of less than 600°C in order to avoid an anatase to rutile form conversion, which decreases the metal ~~oxide-s~~ oxide's capacity for adsorption. A simple regeneration wash step using dilute sulfuric acid may also be used to increase the lifetime of TiO<sub>2</sub> adsorbents when the contacting step 4 is carried out at a high pH. When using a pH greater than 7, an additional step of acid washing the adsorbent is desirable. Regeneration of a manganese dioxide adsorbent has also been demonstrated at 575°C for 15 minutes.

### EXAMPLE

This example illustrates the process of removing phenolic compounds from an aqueous biomass hydrolysis liquor using TiO<sub>2</sub> as the metal oxide. The hydrolysis liquor was an acid

hydrolyzate of hybrid yellow poplar. In this example the following three samples were prepared.

Sample No. 1 was prepared by mixing a 50 ml aliquot, of a well mixed hydrolysis liquor containing a larger amount of suspended solids, in contact with 10 grams of Norton high-surface-area  $\text{TiO}_2$ , in a 100 ml beaker. The sample was agitated by hand for approximately 5 minutes. until the mixture became clear (colloidal particulates deposited on the surface of the  $\text{TiO}_2$ ). The mixture was allowed to settle at room temperature for 1 hour. The  $\text{TiO}_2$  mixture was filtered through a glass Watman GFC filter and the filtrate was stored in a glass container.

Samples Nos. 2 and 3 were prepared by mixing a 50 ml aliquot, of a well-mixed hydrolysis liquor again containing a large amount of suspended solids, in contact with 10 grams of high surface area  $\text{TiO}_2$  in a 100 ml beaker. Unlike sample No. 1, the  $\text{TiO}_2$  in sample No. 2 was left in solution without stirring at room temperature for 8 hours (sample No. 2) prior to the removal of the  $\text{TiO}_2$  phenolic-adsorption-complex, by gravity filtration. Half of the liquid (20 ml) was decanted and filtered for analysis, and the other half of the solution was retained in contact with the  $\text{TiO}_2$  overnight (sample No. 3). The beaker was covered with aluminum foil to minimize evaporation. After 20 hours, the remaining liquid of sample No. 3, was decanted from the  $\text{TiO}_2$  complex and filtered through a Watman GFC glass filter. The filtrates for each sample were diluted in dilute  $\text{H}_2\text{SO}_4$  and analyzed for their phenol concentrations by measuring UV absorbency at 204 nm. In addition, the glucose concentration of the filtrate was measured for each sample using a Yellow Springs Instruments glucose analyzer.

The results of this example are summarized in Table 1. In the table, most of the adsorption occurs within the first hour and very little change is observed in either adsorption or selectivity with prolonged exposure. The absorbance at 204 nm (measured using a ultra-violet/visible spectrometer) reflects the concentration of the phenolic compounds remaining in the treated liquor. The absorbance at 282 nm reflects the concentration of furfural and 5-(hydroxymethyl) furfural. The dilution factor (D) was the dilution used to bring the solution to a concentration where the absorbency is proportional to the concentration.